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(54) Method for preparing shaped articles of vinyl chloride resins with a hydrophilic surface

(57) The surface of a vinyl chloride polymer article is rendered hydrophilic and antistatic in the plasma chamber of an apparatus for plasma generation having a grounded electrode and a power-input electrode inside the plasma chamber in which the temperature of the shaped article T_1 in °C and the temperature of the power-input electrode T_2 in °C are controlled during the plasma treatment to satisfy the relationship:

$$20 - \frac{1}{5} T_1 \leq T_2,$$

the temperature T_1 being in the range from 0 to 80°C and the temperature T_2 not exceeding 100°C.

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SPECIFICATION

Method for preparing shaped articles of vinyl chloride resins with a hydrophilic surface

The present invention relates to the preparation of a shaped article of a vinyl chloride-based resin having a hydrophilic surface.

As is well known, one of the disadvantages of shaped articles of vinyl chloride-based resins is that their surfaces are readily charged with static electricity due to the remarkably hydrophobic or moisture repellent nature inherent in their surfaces. This phenomenon of charging with static electricity is sometimes undesirable because of the poor printability of the surface. Also, the statically charged surfaces are subject to increased deposition of dust and dirt resulting in a less pleasant appearance of the articles.

In order to overcome the above disadvantage of shaped articles of a vinyl chloride-based resin, there has been proposed a method for rendering the surface of the article hydrophilic and antistatic, in which the surface of the article is exposed to an atmosphere of low temperature plasma. This method is indeed effective to some extent as an antistatic treatment and as a means to improve the printability of the surface.

Unfortunately, the above method of plasma treatment has not yet been established as a large-scale treatment method of vinyl chloride-based resin articles. This is partly due to poor reproducibility in the effectiveness of the method even with the most careful control of several parameters which had been thought to influence the effect of the plasma treatment such as the pressure of the gaseous atmosphere, flow rate of the plasma gas, electric power for generating the plasma and the like. This problem of poor reproducibility and low reliability of the method is not limited to the case where the treatment is carried out batch-wise but also occurs in the case where shaped articles are treated in a continuous process. Accordingly, ways have been sought of developing an improved method for the anti-static treatment of shaped articles of vinyl chloride-based resins with low temperature plasma which is capable of giving reproducible results.

The present invention has been established as a result of extensive investigations undertaken by the inventors and is based on the unexpected discovery that the most important parameter influencing the reproducibility of the effectiveness of the plasma treatment for rendering the surface of the resin article hydrophilic is the relationship between the temperatures of the shaped article under treatment and the power-input side electrode installed in the apparatus for generating low temperature plasma.

Thus, the method of the invention for the preparation of a shaped article of a vinyl chloride-based resin having a hydrophilic surface comprises the steps of

(a) placing the shaped article on the grounded electrode installed in the plasma chamber of an apparatus for generating low temperature plasma equipped with a grounded electrode and a power-input electrode inside the plasma chamber,

(b) generating low temperature plasma in the plasma chamber of the apparatus by supplying an electric power to the electrodes so as that the surface of the shaped article is exposed to low temperature plasma of an inorganic gas under a pressure in the range from 0.01 to 10 Torr while the temperature of the shaped article under treatment T_1 in °C and the temperature of the power-input electrode T_2 in °C satisfy the relationship:

$$20 - \frac{1}{5}T_1 \leq T_2$$

the temperature T_1 being in the range from 0 to 80°C and the temperature T_2 not exceeding 100 °C.

Preferred embodiments of the invention will now be described.

The shaped articles of vinyl chloride-based resins to which the method of the present invention is applicable include both rigid or unplasticized ones and flexible or plasticized ones. The vinyl chloride-based resin used as the main component of the shaped article may be either a homopolymeric polyvinyl chloride resin or a copolymer mainly composed of vinyl chloride in a weight ratio of, say, 50 % or more. The copolymers of vinyl chloride are exemplified by copolymers of vinyl chloride and vinyl acetate, copolymers of vinyl chloride and ethylene, copolymers of vinyl chloride and propylene, copolymers of vinyl chloride and acrylonitrile, copolymers of vinyl chloride and styrene, copolymers of vinyl chloride and vinylidene chloride and ternary copolymers of vinyl chloride, styrene and butadiene as well as those graft copolymers mainly composed of polyvinyl chloride. The vinyl chloride-based resin may be a polymer blend of two or more of the above named resins.

Further, the vinyl chloride-based resin may be blended with a minor amount of one or more non-vinyl chloride resins such as copolymers of ethylene and vinyl acetate, copolymers of acrylonitrile and butadiene, copolymers of styrene and acrylonitrile, ternary copolymers of methyl methacrylate, styrene and butadiene, ternary copolymers of acrylonitrile, styrene and butadiene, elastomeric copolymers of ethylene and propylene, ternary elastomeric copolymers of ethylene, propylene and a dienic monomer, polyamide resins, polymers of caprolactam, epoxy-modified polybutadienes, epoxy-modified polyols, organopolysiloxanes and the like.

In addition to the above described resinous constituents, the shaped articles may contain other additive ingredients conventionally used in shaping vinyl chloride-based resins according to need including plasticizers, stabilizers, lubricants, fillers, pigments, dyes, ultraviolet absorbers, anti-oxidants, crosslinking

agents, crosslinking accelerators, cationic, anionic, non-ionic and amphoteric surface active agents and the like.

The shape of the articles of the vinyl chloride-based resins is not particularly important insofar as uniformity in the effect of the plasma treatment can be ensured, and includes films, sheets, tubes and hoses as well as other shapes of irregular forms. The method of shaping the articles may also be a conventional one including extrusion molding, injection molding, calendering, inflation method, compression molding and the like according to the desired shape of the articles and the types of resin to be molded.

The shaped article thus obtained is then subjected to the treatment with low temperature plasma of an inorganic gas under a low pressure in the plasma chamber of an apparatus for generating low temperature plasma. It is necessary that the plasma-generating apparatus used is of the type provided with a grounded electrode and a power-input electrode inside the plasma chamber. Further, it is an essential condition that the temperature of the shaped article under treatment T_1 in °C and the temperature of the power-input electrode T_2 in °C satisfy the following relationship:

$$20 - \frac{1}{5}T_1 \leq T_2,$$

the temperature T_1 being in the range from 0 °C to 80 °C and the temperature T_2 not exceeding 100 °C. When the above relationship is not satisfied, the effectiveness of the hydrophilic treatment does not have good stability and reproducibility.

In the plasma-generating apparatus used in the method of the invention the electrodes are installed inside the plasma chamber so that the electrodes are in contact with the inorganic plasma gas and the inorganic plasma gas introduced into the plasma chamber at a low pressure is converted to low temperature plasma in the vicinity of the electrodes and acts on the surface of the shaped article of the vinyl chloride-based resin placed in the plasma chamber producing the desired effect of imparting affinity for water to the surface of the shaped article.

The form of the power-input electrode is not particularly important and may be suitably selected from flat plate-like, net-like, coil-like and rod-like forms. It is a necessary condition, however, that provision is made for controlling the temperature of the electrode. For example, an electrode provided with a liquid passage for a heating or cooling medium inside it can satisfactorily be used for such a purpose.

The most convenient way for controlling the temperature of the shaped article under plasma treatment is that the article is placed on the grounded electrode in direct contact therewith, the grounded electrode being made of a metal in the form of a flat table-like configuration and provided with a means for temperature control similarly to the power-input electrode. When the shaped article to be treated is a tubular body of continuous length and is to be continuously treated with low temperature plasma, the temperature of the tubular shaped article may be maintained at the desired temperature by passing a heating medium at a predetermined temperature through the tubular article.

Low temperature plasma is readily produced in the plasma chamber of the apparatus by introducing an inorganic plasma gas into the chamber under a low pressure and supplying a high frequency electric power of, for example, from 10 to 700 watts at a frequency of 13.56 MHz between the electrodes. The time required for obtaining sufficient effects of the plasma treatment naturally depends on various parameters including the electric power for the plasma generation and the like but a time of a few seconds to several tens of minutes is usually sufficient. The frequency band of the electric discharge for generating low temperature plasma in the plasma chamber may be low frequency, microwaves, direct current and the like in addition to the above mentioned high frequency.

The inorganic gas for the plasma atmosphere is exemplified by helium, neon, argon, nitrogen, nitrous oxide, nitrogen dioxide, oxygen, air, carbon monoxide, carbon dioxide, hydrogen and chlorine as well as hydrogen chloride, sulfur dioxide, hydrogen sulfied and the like. These inorganic gases may be used either as a single component gas or as a mixture of two or more according to need.

The pressure of the inorganic plasma gas in the plasma chamber is not particularly critical insofar as a stable plasma discharge can be obtained in the chamber. In this regard, a pressure in the range from 0.01 to 10 Torr or, preferably, from 0.01 to 1.0 Torr is usually satisfactory.

Using the plasma treatment in the manner described above, the desired modification of the surface properties of the shaped articles of vinyl chloride-based resins can be achieved with high efficiency and good reproducibility.

The method of the present invention will now be described in further detail by way of examples.

Example 1.

A sheet of a vinyl chloride resin having a thickness of 0.5 mm was fabricated by milling a compounded mixture composed of 100 parts by weight of a homopolymeric polyvinyl chloride resin (TK-1000, a product of Shin-Etsu Chemical Co., Japan) 2 parts by weight of a calcium-zinc-based stabilizer and 3 parts by weight of an epoxy stabilizer in a roller mill at 170 °C for 10 minutes followed by compression molding at 180 °C.

A piece of this sample sheet was placed on a table-like grounded electrode made of a metal in the plasma chamber of an apparatus for generating low temperature plasma and the pressure in the plasma chamber

was maintained at 0.5 Torr by passing a gaseous mixture of carbon monoxide, argon and nitrogen in a 8:1:1 ratio by volume. Both the grounded electrode and the power-input electrode were provided with a liquid passage for passing a heating medium and their temperatures were controlled by this means as indicated in Table 1 below. The temperature of the sample sheet under treatment with the plasma was substantially identical with that of the grounded electrode on which the sample sheet was placed.

Low temperature plasma was generated in the plasma chamber by the application of a high frequency electrical power of 500 watts at 13.56 MHz between the electrodes so that the surface of the sample sheet was exposed to low temperature plasma for 3 minutes.

Each of the sample sheets obtained by the plasma treatment with various combinations of the temperatures of the sample sheet and the power-input electrode was subjected to measurement of the contact angle of water at 25 °C as the most pertinent parameter representing the hydrophilic nature of the surface. The results are set out in Table 1. The contact angle of water on the same sheet without the plasma treatment was 95 at 25 °C.

TABLE 1

(Contact angle of water, degrees)

Temperature of sample sheet T_1, °C	Temperature of power-input electrode T_2, °C							
	0	6	10	14	18	22	50	100
-10	90	90	92	91	94	93	90	91
0	96	90	90	90	62	28	20	38
10	94	89	90	82	35	24	18	36
20	94	89	78	65	25	20	18	34
40	88	78	66	26	21	20	24	34
60	70	63	30	24	21	25	25	39
80	67	29	28	24	21	23	24	39
90	93	93	91	90	92	92	93	94

Example 2

A sheet of a vinyl chloride-based resin having a thickness of 0.5 mm was prepared by milling a compound mixture composed of 50 parts by weight of a hompolymeric polyvinyl chloride resin (TK-1300, a product of Shin-Etsu Chemical Co.), 50 parts by weight of a copolymeric resin containing 12 % by weight of vinyl acetate and 88 % by weight of vinyl chloride (SC-4000, a product of the same company, supra), 1.3 parts by weight of a tin-calcium-based stabilizer and 1 part by weight of an epoxy stabilizer in a roller mill at 160 °C for 10 minutes followed by compression molding at 160 °C.

The treatment of this sample sheet with low temperature plasma was undertaken in a manner similar to Example 1 with various combinations of the temperatures of the sample sheet and the power-input electrode. The pressure of the plasma atmosphere in this case was kept at 0.1 Torr by passing argon gas under reduced pressure. The time of the treatment was decreased to 2 minutes instead of 3 minutes in Example 1 for each piece of the sample sheets.

The thus plasma-treated sample sheets were subjected to an evaluation of the anti-static effect by the measurement of the electrostatic charge voltage induced by rubbing. The measurement of the static voltage was performed by use of a rotary static tester manufactured by Koa Shokai Co. with a cotton cloth for rubbing under a load of 200 g for 30 seconds at 750 r.p.m. in an atmosphere of 50 % relative humidity at 25 °C. The results are summarized in Table 2. The value of the static voltage without the plasma treatment was 8200 volts.

TABLE 2

(Static voltage by rubbing, volts)

Temperature of sample sheet T_1, °C	Temperature of power-input electrode T_2, °C							
	0	6	10	14	18	22	50	100
-10	9050	9000	8200	8150	8000	8750	8400	7950
0	8100	7700	7650	7650	7500	1900	1200	4800
20	7850	770	7600	7600	1850	1700	870	4600
40	7800	7600	7550	1750	1700	1600	850	4100
60	7000	5500	1900	1750	1600	1550	660	3600
80	6900	1800	1700	1600	1600	1400	420	3500
90	8900	8800	8800	8350	8450	8400	8700	9100

Example 3

Twenty sample pieces were taken from the resin sheet prepared in Example 1. These sample pieces were each subjected to the treatment with low temperature plasma in the manner similar to Example 1, in which the plasma atmosphere was an argon atmosphere at 0.3 Torr and the electric power was increased to 700 watts with a shortened treatment time of 1 minute.

The plasma treatment of ten of the above twenty sample pieces was carried out by controlling the temperature of the sample sheet and the power-input electrode both at 40 °C while the plasma treatment of the other ten sample sheets was carried out without temperature control.

These plasma-treated sample sheets were subjected to measurements of the contact angle of water at 25 °C and the static voltage by rubbing, under the same conditions as in Examples 1 and 2, respectively. The results are set out in Table 3.

TABLE 3

	Temperature control	Sample No. 1	2	3	4	5	6	7	8	9	10
Contact angle of water, degrees	Yes	26	24	20	22	18	25	18	20	24	25
	No	39	24	55	75	70	68	25	28	69	75
Static voltage rubbing,	Yes	920	770	820	840	760	770	620	650	900	850
Volts	No	890	1800	4200	5200	900	840	6200	3800	4400	2600

As is clear from the results in Table 3, the temperature control during the plasma treatment is very effective not only in enhancing the affinity of the surface to water but also in giving a good reproducibility of the effectiveness of the treatment.

CLAIMS

1. A method for imparting affinity to water to the surface of a shaped article of a vinyl chloride-based resin which comprises
(a) placing the shaped article in a plasma chamber of an apparatus for generating low temperature plasma provided with a grounded electrode and a power-input electrode inside the plasma chamber, and
(b) generating low temperature plasma in the plasma chamber in an atmosphere of an inorganic gas under a pressure in the range from 0.01 to 10 Torr so as that the surface of the shaped article is exposed to the low temperature plasma while the temperature of the shaped article T_1 in °C and the temperature of the power-input electrode T_2 in °C are controlled to satisfy the relationship:

$$20 - \frac{1}{5}T_1 \leq T_2,$$

the temperature T_1 being in the range from 0 to 80 °C and the temperature T_2 not exceeding 100 °C.

2. The method as claimed in claim 1 wherein both of the grounded electrode and the power-input electrode are provided with a means for temperature control and the shaped article is placed on the grounded electrode.

3. The method as claimed in claim 1, substantially as described in any of the Examples.

4. A shaped article of vinyl-based resin which has been treated by a method according to any preceding claim.

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